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## Changing supersites: assessing the impact of the southern UK EMEP supersite relocation on measured atmospheric composition

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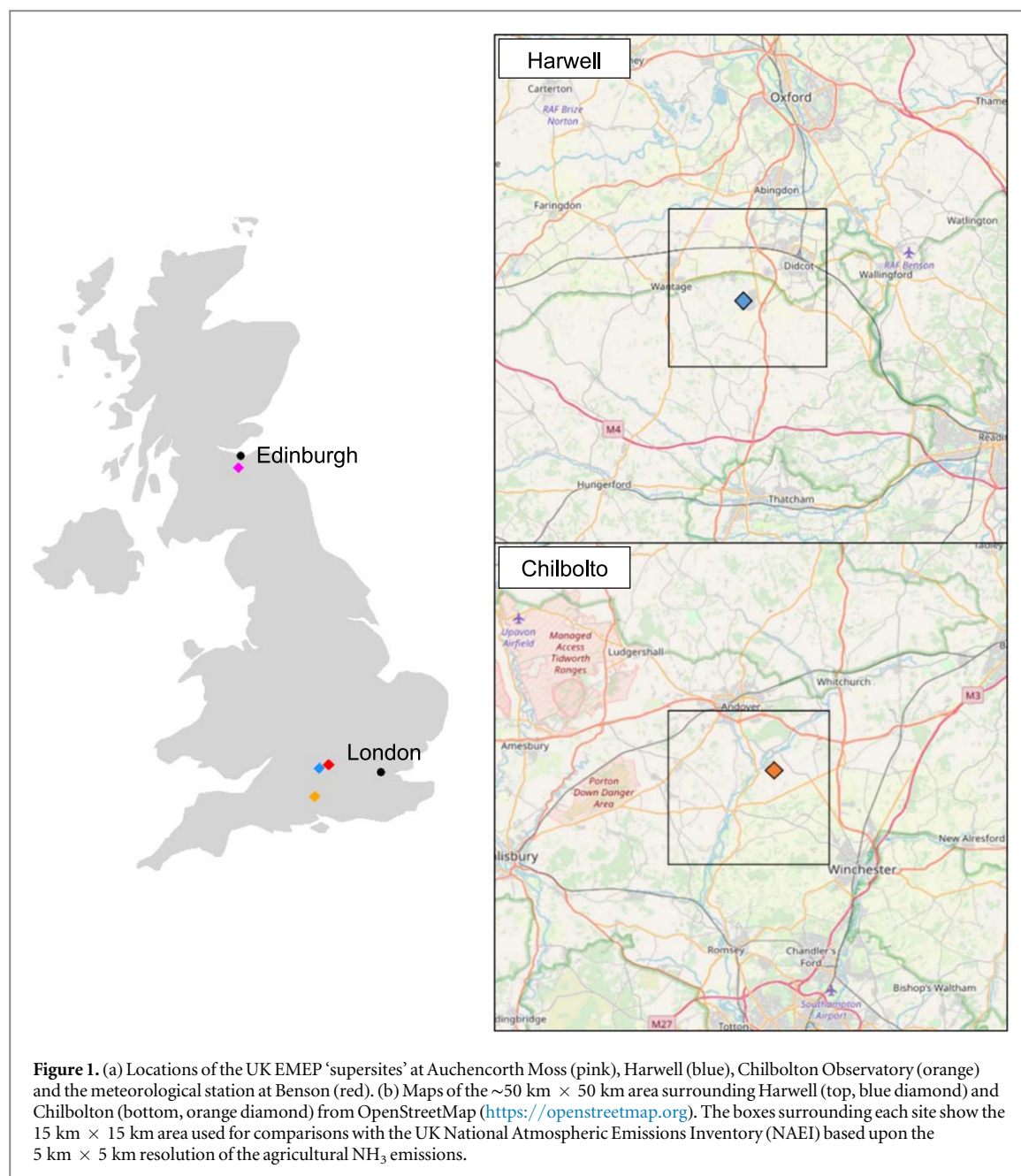
## Abstract

In January 2016 the United Kingdom's southern European Monitoring and Evaluation Programme (EMEP) level-2 air pollution monitoring 'supersite' was relocated from Harwell, Oxfordshire to Chilbolton Observatory, Hampshire. As no co-location study was undertaken, this work retrospectively investigates whether the supersite relocation has led to discontinuities in the time series of concentrations of commonly studied gaseous pollutants ( $\text{NO}_x$ ,  $\text{NH}_3$ ,  $\text{SO}_2$  and  $\text{O}_3$ ) and particulate matter ( $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ ). Two years of measurements pre- and post-relocation (2014–15 and 2016–17 respectively) were analysed in conjunction with meteorological variables and local emission data. The *deweather* package was applied to the concatenated time series to minimise the influence of meteorology. Similar average concentrations of  $\text{PM}_{2.5}$ ,  $\text{PM}_{10}$ ,  $\text{SO}_2$  and  $\text{O}_3$  were observed, but there were substantial differences in that of  $\text{NO}_x$  and  $\text{NH}_3$  (increase by factors of  $\sim 1.6$  and  $\sim 3$ , respectively). The considerably higher  $\text{NH}_3$  concentrations at Chilbolton are attributed to the close proximity of mixed farmland, in particular to a strong south-westerly source contributing to  $\sim 50\%$  of the annual average.  $\text{NO}_x$  and PM concentrations in easterly winds arriving at Chilbolton are  $\sim 2.7$  and  $\sim 1.5$  times larger than at Harwell, from sources including the M3 motorway and Greater London. Westerly concentrations of  $\text{NO}_x$  remain similar, therefore despite a higher frequency of westerly wind, annual mean concentrations are larger. Lower concentrations of PM arriving from the west result in similar annual averages. The secondary inorganic and black carbon components of PM were broadly similar between the sites. The differences in average  $\text{NO}_x$  and  $\text{NH}_3$  at Chilbolton must be taken into account when considering long-term regional trends based on the southern UK supersite data.

## 1. Introduction

Atmospheric pollution has a significant influence on human and ecosystem health. Inhalation of ozone ( $\text{O}_3$ ) and particulate matter has been linked to cardiovascular and respiratory diseases (WHO 2006, 2013). Deposition of acidic gases causes acidification of terrestrial and aquatic ecosystems, and nitrogen deposition (e.g. from nitrogen oxides,  $\text{NO}_x$ , or ammonia,  $\text{NH}_3$ ) leads to eutrophication (Sutton *et al* 2011, RoTAP 2012).

Monitoring of air pollutant concentrations is important for quantifying these effects and their spatio-temporal trends (Fagerli and Aas 2008, Malley *et al* 2016). In Europe, the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP, [www.emep.int](http://www.emep.int)) has the aim of providing member states with this quantitative information (Tørseth *et al* 2012). Measurements within EMEP are made at rural sites representative of the surrounding area (Spangl *et al* 2007, Joly and Peuch 2012) and adhere to prescribed sampling methods and siting criteria detailed by the Chemical



Coordinating Centre (EMEP-CCC) to ensure comparability (Kuhlbusch *et al* 2014). Spatially distributed sites provide data for evaluation of regional models (Fagerli and Aas 2008, Cape 2009, Malley *et al* 2014), whilst hourly measurements for 40+ years allow characterisation of emission patterns and separation of long-term trends from interannual variability (Tørseth *et al* 2012). Such data help establish achievable mitigation strategies (Pope and Wu 2014) and track impacts of implemented measures.

The UK has been a member of EMEP since its inception in 1979, and currently operates two level-2 ‘supersites’ (UNECE 2004a, 2004b) at Auchencorth Moss in southern Scotland, and Chilbolton Observatory in southern England (Defra 2018a, 2018b; figure 1) measuring a wide range of pollutants. The southern supersite, Chilbolton, opened in January 2016 following the closure of the previous site (Harwell, figure 1) in December 2015, which had been active for several decades. The aim of this study is to investigate whether the move from Harwell to Chilbolton led to a temporal change in the chemical climate recorded by the southern rural UK supersite. Given the extensive instrumentation, duplicate measurements could not be run for any overlap period. An analysis is presented of measurements in the years directly pre- and post-relocation (2014–15 and 2016–17 respectively), focussing on nitrogen oxides ( $\text{NO}_x$ ), ammonia ( $\text{NH}_3$ ), sulphur dioxide ( $\text{SO}_2$ ), particulate matter  $<10$  and  $2.5 \mu\text{m}$  in diameter ( $\text{PM}_{10}$  and  $\text{PM}_{2.5}$ , respectively) and ozone ( $\text{O}_3$ ).

**Table 1.** Annual mean concentrations (with 95% confidence intervals) and annual percentage data capture of measurements for the investigated species at Harwell (2014–15), and Chilbolton (2016–17).

		Annual mean concentration $\pm$ 95% confidence intervals/ $\mu\text{g m}^{-3}$ (Data capture/%)			
Species	Instrument	Harwell 2014	Harwell 2015	Chilbolton 2016	Chilbolton 2017
SO <sub>2</sub>	Monitor for AeRosols and Gases in Air (MARGA)	0.245 $\pm$ 0.028 (94%)	0.150 $\pm$ 0.0027 (70%)	0.157 $\pm$ 0.0044 (58%)	0.131 $\pm$ 0.0032 (79%)
HONO		0.464 $\pm$ 0.0068 (94%)	0.340 $\pm$ 0.0049 (70%)	0.494 $\pm$ 0.011 (58%)	0.454 $\pm$ 0.008 (79%)
HNO <sub>3</sub>		0.159 $\pm$ 0.0029 (94%)	0.138 $\pm$ 0.0032 (68%)	0.159 $\pm$ 0.0050 (57%)	0.162 $\pm$ 0.0037 (80%)
NH <sub>3</sub>		1.96 $\pm$ 0.049 (95%)	2.05 $\pm$ 0.044 (70%)	5.88 $\pm$ 0.22 (54%)	6.23 $\pm$ 0.18 (82%)
Automatic Urban and Rural Network (AURN)					
O <sub>3</sub>	UV absorption	56.0 $\pm$ 0.45 (99%)	57.1 $\pm$ 0.42 (98%)	48.9 $\pm$ 0.53 (97%)	51.5 $\pm$ 0.48 (98%)
NO <sub>x</sub>	Chemiluminescence	10.5 $\pm$ 0.30 (97%)	9.20 $\pm$ 0.22 (97%)	18.5 $\pm$ 0.49 (91%)	13.8 $\pm$ 0.35 (97%)
NO <sub>2</sub>		7.99 $\pm$ 0.20 (97%)	7.68 $\pm$ 0.16 (97%)	14.3 $\pm$ 0.25 (91%)	11.2 $\pm$ 0.19 (97%)
PM <sub>10</sub>	TEOM-FDMS	14.3 $\pm$ 0.27 (74%)	15.1 $\pm$ 0.21 (89%)	14.9 $\pm$ 0.25 (85%)	13.3 $\pm$ 0.19 (98%)
PM <sub>2.5</sub>		9.06 $\pm$ 0.19 (96%)	8.55 $\pm$ 0.17 (96%)	9.45 $\pm$ 0.19 (93%)	7.38 $\pm$ 0.17 (98%)
SO <sub>2</sub>	UV fluorescence	1.01 $\pm$ 0.054 (98%)	0.939 $\pm$ 0.013 (93%)	0.876 $\pm$ 0.017 (64%)	0.763 $\pm$ 0.013 (89%)

## 2. Method

### 2.1. Site details

The Harwell supersite is predominantly surrounded by agricultural land near Didcot, Oxfordshire (lat: 51.571°, lon: −1.325°, altitude: 126 m), 70 km west of London and 20 km south of Oxford (figure 1). The closest minor road is ~400 m to the west and a dual-carriageway (A34) ran ~2 km to the east. The town of Didcot is ~6.4 km to the north-east. Approximately 8 km in the same direction was a coal and oil fired power station ('Didcot A'), formerly a nearby major point source of NO<sub>x</sub> and SO<sub>2</sub> (Abdalmogith and Harrison 2006, Vieno *et al* 2010), that closed on 22nd March 2013 and was demolished in 2016. 'Didcot B', a natural gas power plant on the same site, remains operational. Measurement of atmospheric pollutants at Harwell started in 1976 (UKEAP 2015) prior to its incorporation as an EMEP level-2 supersite (UNECE 2004b). Operations ceased on 31st December 2015.

The Chilbolton Observatory site is located ~50 km south of Harwell in an agricultural (mainly arable) landscape, ~200 m south-east of the edge of Chilbolton village, Hampshire (lat: 51.150°, lon: −1.438°, altitude: 78 m) and 100 km south-west of London (Defra 2018b). Two single-carriageway main roads run ~1 km to the west (A3057), and ~3 km to the south (A30) (figure 1). The site began monitoring as an EMEP level-2 supersite on 11th January 2016, after instrument relocation from Harwell.

### 2.2. Measurement data

The full suite of measurements at the two sites is summarised in UK Eutrophying and Acidifying Pollutants (UKEAP) network reports (UK-AIR Library 2018), a subset of which are investigated in this work (table 1, and supplementary information figure S1 is available online at [stacks.iop.org/ERC/1/041001/mmedia](https://stacks.iop.org/ERC/1/041001/mmedia)). Concentration data were downloaded from the UK Department for Environment, Food and Rural Affairs (Defra) online data repository (UK-AIR Data Selector 2018).

Data are evaluated here for the two years either side of site relocation (Harwell 2014–15 and Chilbolton 2016–17, respectively). Data capture statistics are given in table 1. O<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub>, PM<sub>10</sub> and PM<sub>2.5</sub> measurements derive from the UK Automatic Urban and Rural Network (AURN). Instrumentation selection, calibration and data ratification follow EU Air Quality Directives (2008/50/EC), and data are archived as hourly averages (UK-AIR Library 2018). Hourly measurements of NH<sub>3</sub> and other trace gases, together with water-soluble ions within PM<sub>2.5</sub> and PM<sub>10</sub>, are provided by the Monitor for AeRosols and Gases in Air (MARGA) instrument (EMEP 2007, Stieger *et al* 2018) with data quality assurance processes as described in Twigg *et al* (2015).

Hourly meteorological data comprise on-site measurements at Harwell and Chilbolton (Wrench). Data were also downloaded for the meteorological station at Benson, Oxfordshire (lat: 51.616°, lon: −1.096°, altitude: 57 m), marked on figure 1(a), from the NOAA Integrated Surface Database using the *worldmet* package (Carslaw 2018, NOAA 2018) for the full time period being considered. These data were used to validate the use of concatenated meteorological time series from the two supersites (see supplementary information).

### 2.3. Meteorological detrending

To examine for evidence of a step-change in concentration coincident with site relocation, the *deweather* function (Carslaw 2017) was applied to concatenated Harwell and Chilbolton datasets (2014–17) in a technique



known as ‘meteorological normalisation’ (Grange *et al* 2018). This accounts for non-linear and complex relationships between predictors, such as meteorological or temporal variables (Carslaw and Taylor 2009), allowing changes in time series not directly caused by these predictors to be identified. Models are built using a stochastic process that results in reduced variance of the final model (Friedman 2002), but consequently, a slightly different model is produced with each run (Elith *et al* 2008). A set of 10 identically-built *deweather* models were performed for each pollutant time series, using meteorological predictor variables measured at the same site as the pollutants. Further details of the model, including comparisons using different meteorological data, are given in the supplementary information (section S2 and figure S3).

## 2.4. Emission inventories

Annual emission estimates for  $\text{NH}_3$ ,  $\text{NO}_x$ ,  $\text{SO}_2$ ,  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  were obtained from the UK National Atmospheric Emission Inventory (NAEI, <http://naei.beis.gov.uk/>) for both locations. Individual species emissions were taken from the 2015 inventory and were aggregated over the  $15 \text{ km} \times 15 \text{ km}$  area surrounding each site shown in figure 1. The areas were defined according to the gridded agricultural sector  $\text{NH}_3$  emissions which have a spatial resolution of  $5 \text{ km} \times 5 \text{ km}$ , but for all other pollutants the underlying resolution was  $1 \text{ km} \times 1 \text{ km}$ .

## 3. Results and discussion

### 3.1. Overview

Table 1 summarises the annual mean concentration and corresponding 95% confidence interval for each pollutant for each year. Chilbolton MARGA measurements have the lowest data capture (54%–58%) since these measurements did not commence until 11th February 2016, and instrument issues led to missing data between 9th July and 1st September 2016. Between August 2014 and September 2015 a plume from the volcanic eruption at Holuhraun, Iceland, passed over the UK and is observed in the  $\text{SO}_2$  time series (figure S1). Similarly in spring 2014, elevated PM concentrations were caused by a combination of Saharan dust and ammonium nitrate formed from European emissions (Vieno *et al* 2016) (figure S1). Other PM episodes are also apparent between 2014 and 2017 (figure S1), typically accumulating in low wind speeds and lasting no more than a few days (Defra 2015, 2016, 2017).

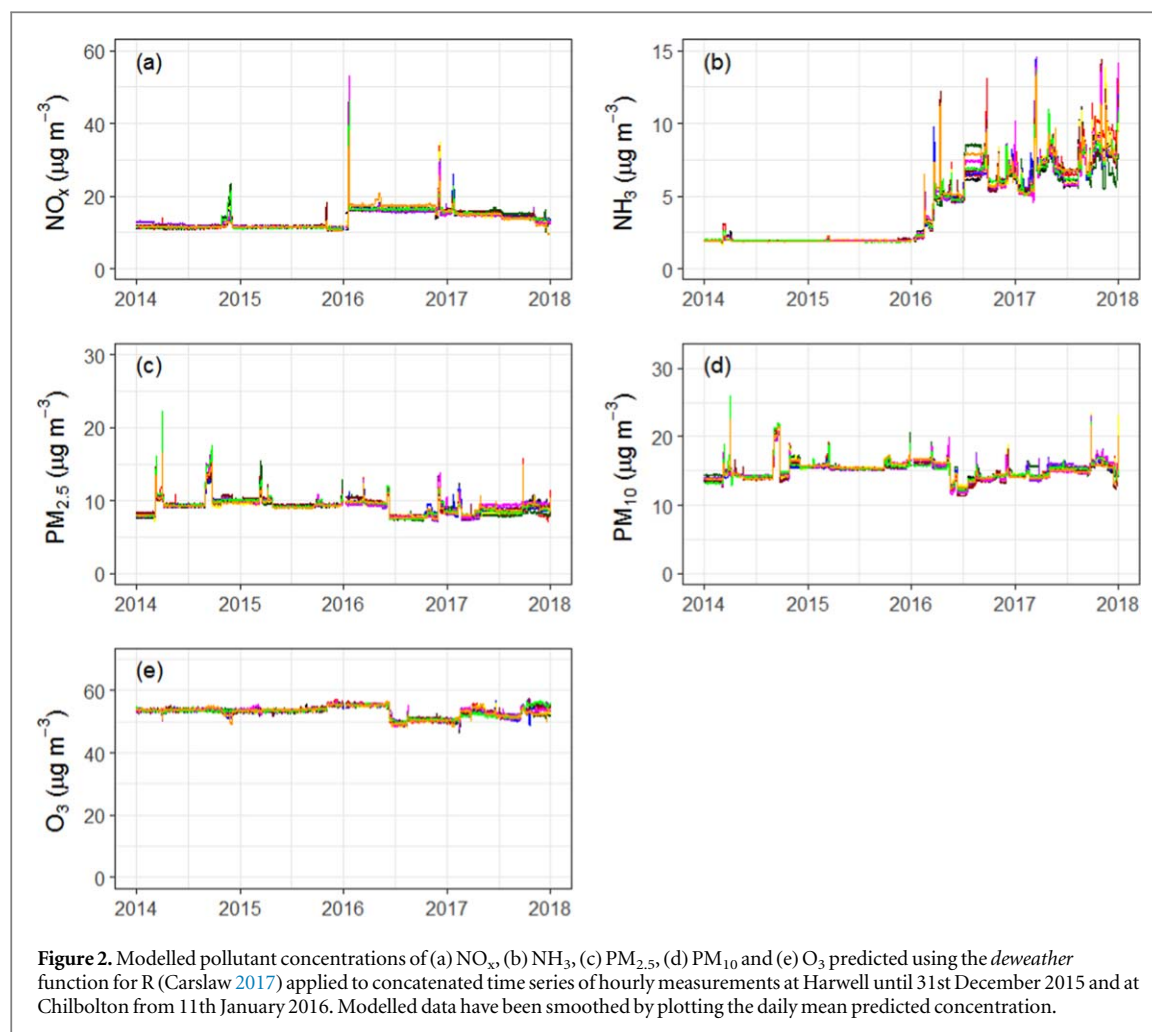
### 3.2. $\text{NO}_x$

The average 2016 and 2017 concentration of  $\text{NO}_x$  at Chilbolton was approximately 1.6 times greater than the average 2014 and 2015 concentration at Harwell (annual means of  $18.5$  and  $13.8 \mu\text{g m}^{-3}$  cf  $10.5$  and  $9.20 \mu\text{g m}^{-3}$  respectively, table 1). The  $\text{NO}_x$  *deweather* time series also shows an abrupt increase coincident in timing with the relocation of the measurement site (figure 2(a)).

In contrast to the greater average  $\text{NO}_x$  concentrations at Chilbolton, the total local  $\text{NO}_x$  emissions integrated over the  $15 \text{ km} \times 15 \text{ km}$  area around Harwell are more than 5 times greater than from the same-size area around Chilbolton (figure 3). The  $\text{NO}_x$  emissions close to Harwell are dominated by specific sources including Didcot town, Didcot B power station in the north-east, and high traffic flow on the dual-carriageway (A34) running north-south 2 km to the east. Across the 225 individual  $1 \text{ km} \times 1 \text{ km}$  grid squares within the area surrounding Harwell, 47% of total local emissions are contributed by the grid square with the highest emissions, whilst the 25 highest emission grid squares contribute 84%. Similar analysis at Chilbolton shows less dominance of local emissions from the single highest (6%) and 25 highest (61%, including part of the A303, ~8 km north) grid squares.

These differences in  $\text{NO}_x$  source configurations are illustrated by pollution wind roses (figure 4). The aforementioned sources north of Harwell generate the most polluted air transported to the site but do not contribute significantly more to the annual average than other directions. Considering  $\text{NO}_x$  to have an atmospheric lifetime of ~4–6 h in the mid-latitudes (Beirle *et al* 2011) and an average wind speed of ~15  $\text{km h}^{-1}$  for southern England (figure S2; Wrench, NOAA 2018), the London pollution plume could plausibly be observed at both sites. It appears Harwell is less influenced by London (~100° bearing) than Chilbolton (~70°), for which this wind direction provides a dominant contribution to the annual average. However, the M3 motorway also contributes  $\text{NO}_x$  to this wind direction, stretching for ~56 km between Chilbolton and London. Traffic along the length of the M3 (~95 km) and other major roads are the probable reason why a larger average concentration of  $\text{NO}_x$  (>2.2 times higher) is observed in easterly (0°–180°) than in westerly winds (181°–360°, table 2). More frequent westerly winds during 2017 led to a reduced annual average compared with 2016 ( $13.8$  cf  $18.5 \mu\text{g m}^{-3}$ ).

The importance of wind direction to  $\text{NO}_x$  concentrations at both sites is reflected in the relative importance of variables used in the *deweather* models (table S2). Wind direction had the largest mean relative importance of



19.1%, closely followed by ambient temperature (18.7%) and (long-term) trend (18.4%). Unsurprisingly, predicted concentrations of  $\text{NO}_x$  are elevated at lower ambient temperatures ( $\leq 10^\circ\text{C}$ ) and during colder months (October–February), as these conditions limit the dispersion of emissions (AQEG 2004), and there is a higher demand for domestic heating. The importance of the trend variable is a consequence of the abrupt increase in  $\text{NO}_x$  at the time of site relocation in the concatenated *deweather* time series (figure 2(a)). This supports the interpretation of a real difference in annual mean  $\text{NO}_x$  concentration between Harwell and Chilbolton.

### 3.3. $\text{NH}_3$

The annual mean  $\text{NH}_3$  concentrations at Chilbolton in 2016 and 2017 ( $5.88$  and  $6.23 \mu\text{g m}^{-3}$  respectively, table 1) are about 3 times higher than at Harwell in 2014 and 2015 ( $1.96$  and  $2.05 \mu\text{g m}^{-3}$ , respectively), the greatest difference of all pollutants investigated. Although data capture at Chilbolton in 2016 was rather low (58%), and most missing data occurred during the summer (figure S1) when  $\text{NH}_3$  concentrations are typically larger (Tang *et al* 2018), therefore the annual average in 2016 is likely biased low by the missing data.

Application of the *deweather* model to the concatenated time series of  $\text{NH}_3$  concentrations (figure 2(b)) confirms a distinct increase in mid-February 2016, coincident with commissioning of the MARGA at Chilbolton. Trend is the dominant variable in the *deweather* model ( $45.5 \pm 0.6\%$ , figure S4 and table S2). The raw time series shows elevated springtime concentrations at Harwell (figure S1), consistent with typical livestock manure and synthetic fertiliser applications observed in NW European springtime (Vieno *et al* 2016). These springtime peaks are mirrored in the predicted concentrations of  $\text{NH}_3$  during 2014 and 2015, and reflected by the partial dependency of the week-of-year variable predicting increased concentrations during Julian weeks 5–20 (figure S4). Following site relocation the *deweather* time series showed  $\text{NH}_3$  concentrations remaining high, with large and infrequent peaks that demonstrate little seasonality. Despite this, maximum hourly  $\text{NH}_3$  at Chilbolton in 2016 and 2017 were during spring ( $126 \mu\text{g m}^{-3}$  on 22nd March 2016 and  $94.4 \mu\text{g m}^{-3}$  on 24th May 2017).

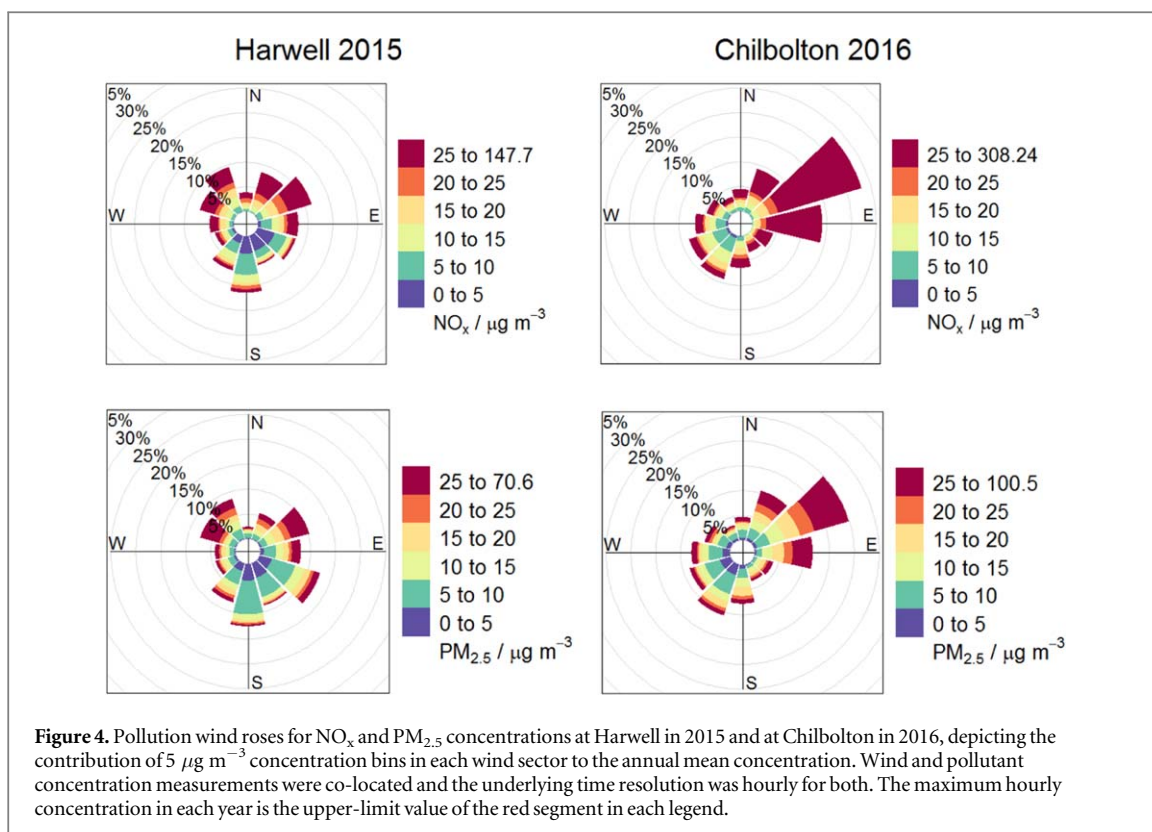


**Figure 3.** The top panel shows annual emissions maps of  $\text{NO}_x$  and  $\text{NH}_3$  from the National Atmospheric Emissions Inventory database (NAEI, <https://naei.beis.gov.uk/>) for the 15 km × 15 km area surrounding Harwell and Chilbolton sites. Underlying data area at 5 km × 5 km grid resolution for agricultural  $\text{NH}_3$ , displayed at 1 km × 1 km resolution. The bar plot in the lower panel displays the total emissions of  $\text{NO}_x$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  for the same area around both sites, whilst the black point indicates the emission from the component grid square with the maximum emission across the contributing grid squares.

Ammonia has a short atmospheric lifetime and high spatial heterogeneity in its sources (Vogt *et al* 2013, Dammers *et al* 2017), so receptor concentrations are significantly influenced by local emissions. The contrasting concentrations at Harwell and Chilbolton are not reflected in the total NAEI estimates of local  $\text{NH}_3$  emissions, which show similar averages over the 15 km × 15 km area surrounding each site (figure 3). However, the total at Harwell includes contribution from a disproportionately large 1 km × 1 km grid square over the site of Didcot B power station, over 3.4 times greater than any other grid square surrounding either site. When emissions from only the agricultural sector are considered, the greatest emissions are associated with the 5 km × 5 km grid square also containing the site, suggesting the presence of a nearby agricultural source or sources.

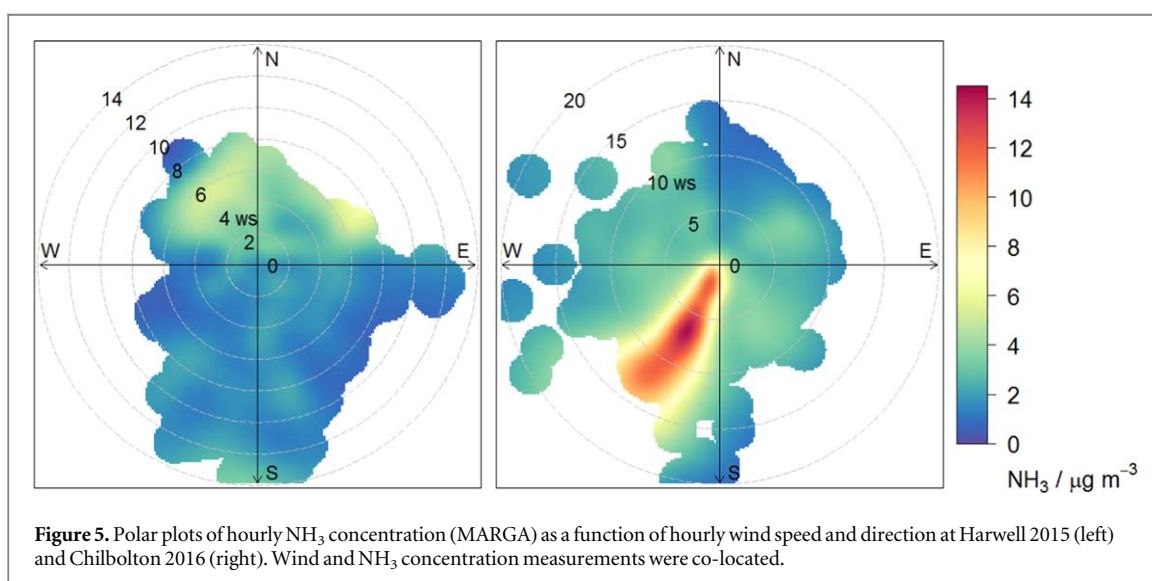
Polar plots of  $\text{NH}_3$  concentration as a function of wind speed and direction for both sites (figure 5) reveal an obvious dominant local source to the south-west of Chilbolton. Figure 6 demonstrates the difference in concentration between this source and background  $\text{NH}_3$  at Chilbolton in 2016, by dividing prevailing wind into four direction sectors: east (E, 30°–180°), south-west (SW, 180°–250°), north-west (NW, 250°–350°) and north (N, 350°–30°). The N sector appears to reflect background  $\text{NH}_3$  levels, with a mean concentration of  $2.2 \mu\text{g m}^{-3}$ , comparable to average  $\text{NH}_3$  concentrations measured at Harwell across all wind directions (figure 5). Mean concentrations in E, NW and SW sectors are higher ( $3.1$ ,  $3.4$  and  $7.1 \mu\text{g m}^{-3}$ , respectively) and demonstrate an inverse relationship with wind speed, suggesting nearby sources at Chilbolton. Approximately 1.5 km from the

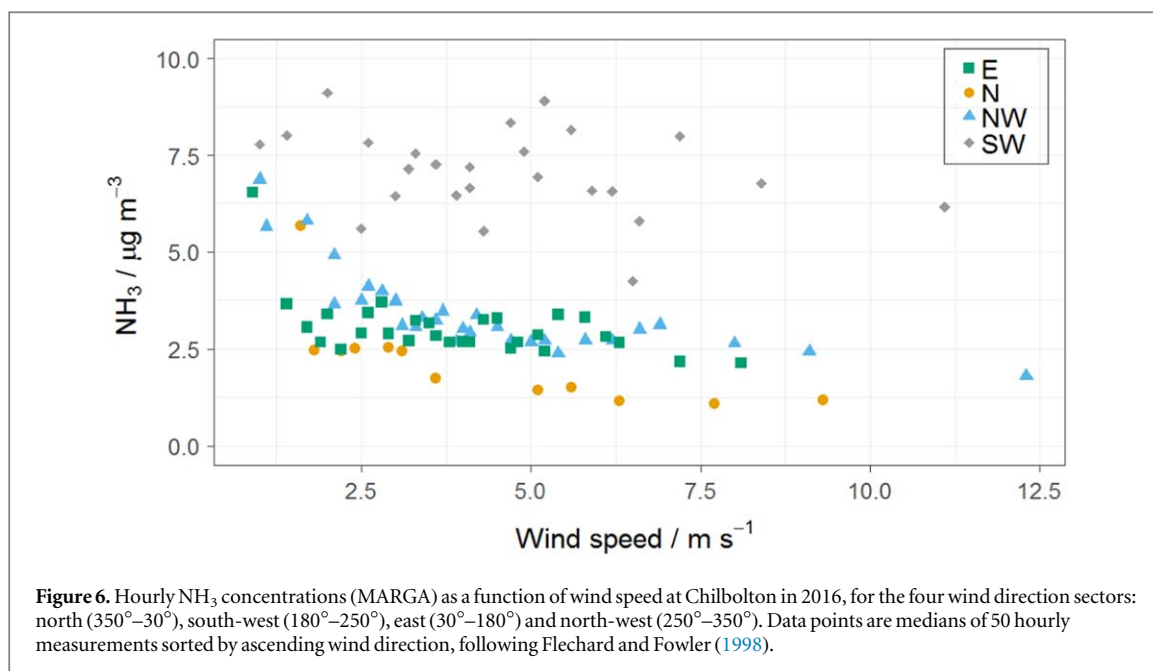




**Table 2.** Annual mean concentrations of hourly NO<sub>x</sub> measurements for easterly (0°–180°) and westerly (181°–360°) wind directions. The remaining percentage of data (% NA) includes hours where NO<sub>x</sub> concentration or wind direction were not recorded.

Site and year	Mean NO <sub>x</sub> concentration / $\mu\text{g m}^{-3}$		Percentage of total annual wind / %		
	Westerly	Easterly	Westerly	Easterly	NA
Harwell 2014	11.1	10.0	39	59	2
Harwell 2015	10.5	8.60	34	55	11
Chilbolton 2016	12.0	28.6	54	35	11
Chilbolton 2017	10.2	22.6	69	28	3





site in the SW sector is the centre of a cattle farm, whilst a further 1.5 km in the same direction is a mushroom farm, likely to release  $\text{NH}_3$  at regular intervals coinciding with mushroom growth cycles (Sather *et al* 2008). For the remaining E/NW sectors,  $\text{NH}_3$  concentrations presumably reflect levels associated with the surrounding intensively managed arable land, which in general are larger emitters than agricultural activities near Harwell.

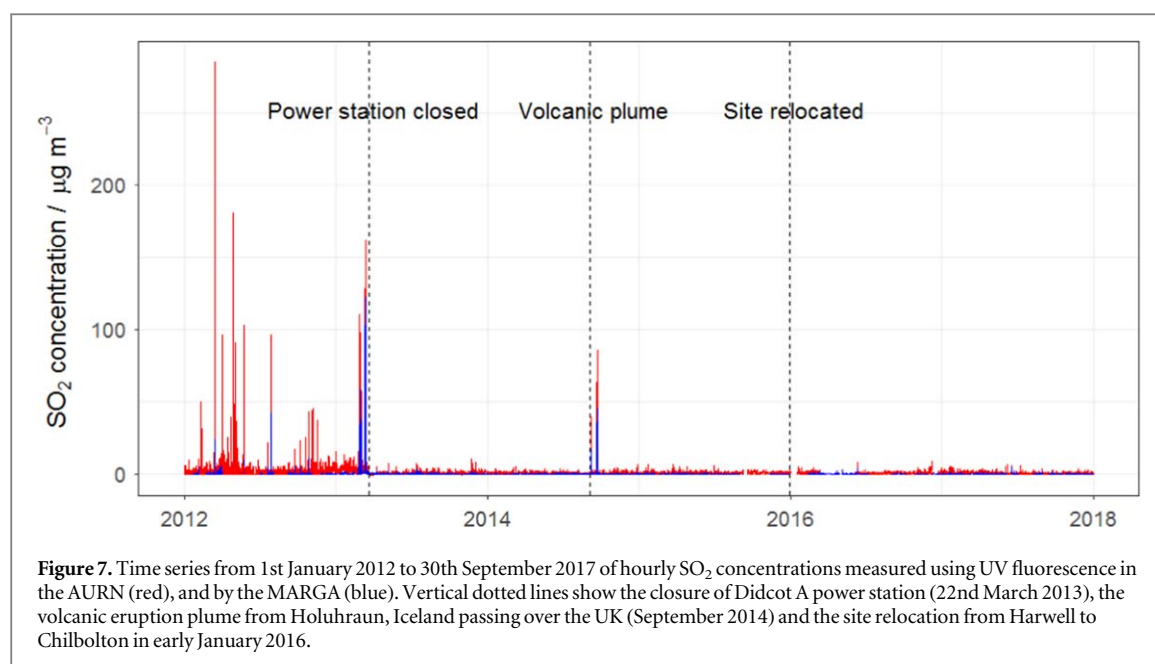
### 3.4. $\text{SO}_2$

Hourly  $\text{SO}_2$  concentrations at both sites are determined by two different measurement methodologies (table 1) but there was poor agreement between them (figure S5). This is anticipated, as the limit of detection (LOD) of the UV fluorescence analyser ( $1.5 \text{ ppb}$ ,  $\sim 4 \mu\text{g m}^{-3}$ ) is approximately two orders of magnitude greater than that of the MARGA ( $0.04 \mu\text{g m}^{-3}$  (Makkonen *et al* 2012)). The aim of the AURN  $\text{SO}_2$  analysers is to detect pollution events (Twigg *et al* 2016) where concentrations could exceed national/EU limit values (hourly and daily means of 350 and  $125 \mu\text{g m}^{-3}$ ), whereas the MARGA is designed to monitor changes in background concentrations of  $\text{SO}_2$ . Extending the time series of  $\text{SO}_2$  measurements at Harwell back to 2012 shows that there was a large reduction in concentrations in early 2013 (figure 7), coincident with the closure of Didcot A coal and oil power station, which whilst operational was one of the largest  $\text{SO}_2$  emission sources in the UK (Vieno *et al* 2010). Following this event there are no discernible changes in  $\text{SO}_2$  concentration, including through the site relocation, apart from a singular peak in August 2014 which can be attributed to an Icelandic volcanic eruption (Twigg *et al* 2016). Whilst the emission inventory estimates greater local  $\text{SO}_2$  emissions around Harwell than around Chilbolton (figure 3), these are overwhelmingly dominated at Harwell by Didcot B power station. The relative infrequency of north-easterly wind to the site, coupled with the elevated source of these emissions, resulted in little influence of Didcot B on ambient measured concentrations. Consequently, there is effectively no change in measured  $\text{SO}_2$  arising from the site relocation.

### 3.5. Particulate matter

Data capture was high for total  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  (table 1), but poorer for the individual species concentrations. Annual mean concentrations of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  were similar at Harwell and Chilbolton (2014 and 2015 average  $\text{PM}_{10} = 14.7 \mu\text{g m}^{-3}$ , 2016 and 2017 average  $\text{PM}_{10} = 14.1 \mu\text{g m}^{-3}$ ; equivalent data for  $\text{PM}_{2.5} = 8.8$  and  $8.4 \mu\text{g m}^{-3}$ ), indicating no substantive change in long-term mean PM concentration at the time of site relocation. There was also no significant difference in the number of  $\text{PM}_{10}$  daily mean exceedances of  $50 \mu\text{g m}^{-3}$  before and after site relocation: twice each year at Harwell, 3 times at Chilbolton in 2016 and once in 2017.

The *deweather* models for both  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  (figures 2(c) and (d)) show temporal variability, but no evidence of a significant step-change in concentration at the time of site relocation. The model predicted lower concentrations of  $\text{PM}_{10}$  in June 2016 because measured values in this period 12th June—31st July 2016 (mean of  $7.6 \mu\text{g m}^{-3}$ ) were substantially lower than the mean for the rest of the time series ( $14.4 \mu\text{g m}^{-3}$ ). There is a similar effect in the modelled  $\text{PM}_{2.5}$  time series. Model disagreement in the latter part of the  $\text{PM}_{2.5}$  *deweather* time series is presumed to be due to the presence of a large measurement value ( $186.8 \mu\text{g m}^{-3}$ , 27th April 2017),



**Figure 7.** Time series from 1st January 2012 to 30th September 2017 of hourly  $\text{SO}_2$  concentrations measured using UV fluorescence in the AURN (red), and by the MARGA (blue). Vertical dotted lines show the closure of Didcot A power station (22nd March 2013), the volcanic eruption plume from Holuhraun, Iceland passing over the UK (September 2014) and the site relocation from Harwell to Chilbolton in early January 2016.

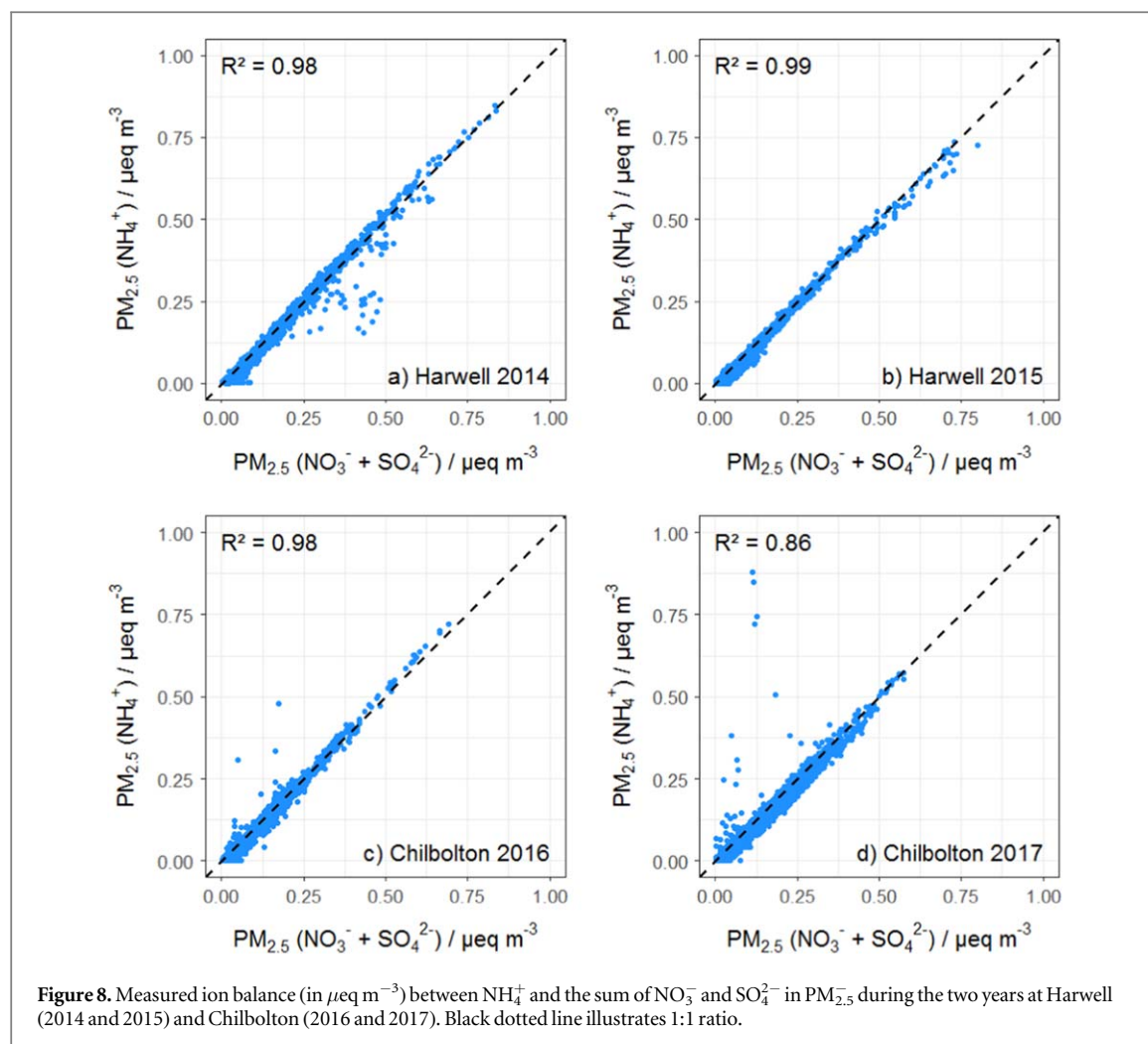
almost twice any other hourly  $\text{PM}_{2.5}$  concentration. The stochastic nature of the *deweather* function resulted in some models being built using this data point, while others were not.

The annual NAEI emissions integrated over the  $15 \text{ km} \times 15 \text{ km}$  area surrounding each site are substantially greater around Harwell than Chilbolton for both  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  (figure 3). Locations of high  $\text{PM}_{2.5}$  emissions within the area surrounding Harwell include those with substantial  $\text{NO}_x$  emissions (Didcot town, Didcot B power station and the A34). The  $25 \text{ km}^2$  grid squares with highest PM emissions around Harwell contribute 63% to the total, whereas the equivalent at Chilbolton contribute 54%. As with  $\text{NO}_x$ , an increase in  $\text{PM}_{2.5}$  concentrations is observed in the prevailing easterly wind at Chilbolton as compared to Harwell ( $13.2$  in 2016 *cf*  $8.1 \mu\text{g m}^{-3}$  in 2015, table S3), however westerly winds have lower concentrations ( $6.8$  *cf*  $9.6 \mu\text{g m}^{-3}$ ), which accounts for the comparable annual averages pre- and post-relocation. The same conclusions apply for  $\text{PM}_{10}$  (figure S6).

Data capture for MARGA measurements were poorer than for TEOM-FDMS measurements (table 1). Nevertheless for all secondary inorganic aerosol (SIA) ions analysed, the data capture rate was sufficient for comparisons of annual measurements (all years  $>58\%$ ). Anthropogenically-derived  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  dominate  $\text{PM}_{2.5}$  at both sites, contributing an average of 58% to total measured mass at Harwell (2014–15) and 59% at Chilbolton (2016–17). The calculated SIA ion balance for  $\text{PM}_{2.5}$  (figure 8) shows good correlation for all years, despite a few events of exception. More acidic aerosols are observed in 2014, with the greatest excess in September where concentrations of  $\text{SO}_4^{2-}$  were significantly elevated from the Holuhraun eruption plume passing over the UK (Twigg *et al* 2016). Both years at Chilbolton exhibit a large excess of basic aerosol on days reaching high  $\text{NH}_4^+$  concentrations ( $8.64$  and  $22.6 \mu\text{g m}^{-3}$  on 22nd March 2016 and 11th March 2017 respectively; table 3). In general, all years appear to have a slight bias towards basic aerosol and are comparable to observations at the northern UK EMEP supersite (Auchencorth Moss; Twigg *et al* 2015). Similar observations apply to the coarse fraction ( $\text{PM}_{\text{coarse}} = \text{PM}_{10} - \text{PM}_{2.5}$ ), where SIA contributes 15% to total aerosol mass at both Harwell (2014–15) and Chilbolton (2016–17). Annual average black carbon measurements (Aethalometer, Black Carbon Network) are comparable at  $\sim 0.40 \mu\text{g m}^{-3}$  between Harwell (2014–15) and Chilbolton (2016–17). Given the comparable total PM at both sites, this indicates that there is also a similar contribution of secondary organic aerosols (SOA) in both fractions.

### 3.6. Ozone

Data capture for hourly  $\text{O}_3$  concentrations was high ( $>98\%$  for each year, table 1). Annual mean concentrations of  $\text{O}_3$  were somewhat lower after the site relocation,  $48.9$  and  $51.5 \mu\text{g m}^{-3}$  for 2016 and 2017 respectively at Chilbolton, compared with  $56.0$  and  $57.1 \mu\text{g m}^{-3}$  for 2014 and 2015 at Harwell (table 1). However, the *deweather* model time series for  $\text{O}_3$  data (figure 2(e)) does not show evidence of a step-change associated with the site relocation (the modelled decrease in mid-2016 is coincident with the similar observation for PM). The slightly lower annual mean background  $\text{O}_3$  at Chilbolton than at Harwell may be due to interannual variability in  $\text{O}_3$ , but the lower background concentration is also consistent with an inverse concentration relationship with the unambiguously higher background  $\text{NO}_x$  at Chilbolton.



**Table 3.** Annual mean particulate  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations measured by MARGA in  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$ . Key: max = maximum hourly measurement of the year,  $\mu_A$  = arithmetic annual mean and  $\sigma_A$  = arithmetic standard deviation across the year.

	2014 $\mu\text{g m}^{-3}$			2015 $\mu\text{g m}^{-3}$			2016 $\mu\text{g m}^{-3}$			2017 $\mu\text{g m}^{-3}$		
	$\text{NH}_4^+$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{NH}_4^+$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{NH}_4^+$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{NH}_4^+$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$
$\text{PM}_{2.5}$												
max	15.2	47.4	29.9	13.2	38.0	13.3	13.0	33.7	9.98	22.6	29.0	13.5
$\mu_A$	1.25	2.62	1.87	0.94	2.33	1.87	1.28	2.98	1.43	1.05	2.78	1.38
$\sigma_A$	1.75	4.17	2.20	1.46	3.95	1.04	1.51	3.78	1.04	1.49	3.69	1.23
$\text{PM}_{10}$												
max	16.0	50.9	31.4	13.8	41.2	13.9	12.8	34.0	9.7	21.6	35.9	15.8
$\mu_A$	1.31	2.97	2.02	0.98	2.65	1.48	1.35	3.50	1.55	1.17	3.37	1.61
$\sigma_A$	1.82	4.42	2.32	1.51	4.17	1.09	1.53	4.04	1.05	1.61	4.15	1.33

## 4. Conclusions

The relocation of the southern UK EMEP supersite from Harwell to Chilbolton in January 2016 has not resulted in discontinuities in average measured concentrations of  $\text{PM}_{2.5}$ ,  $\text{PM}_{10}$ ,  $\text{SO}_2$  and  $\text{O}_3$  (based on two-year pre- and post-relocation time comparisons), but has led to substantial increases in average concentrations of  $\text{NO}_x$  and  $\text{NH}_3$ , by a factor of  $\sim 1.6$  and  $\sim 3$ , respectively.

Concentrations of  $\text{NO}_x$  and PM in easterly wind arriving at Chilbolton are  $\sim 2.7$  and  $\sim 1.5$  times larger than at Harwell, from common sources including the M3 motorway and Greater London. Prevailing winds from the west contribute similar  $\text{NO}_x$  concentrations at both sites, therefore despite a higher frequency of westerly wind at Chilbolton, the larger easterly concentrations result in larger annual means. Westerly winds carry lower concentrations of PM to Chilbolton than Harwell, thereby resulting in similar annual averages. Measurements show no substantive difference in the contribution of secondary inorganic aerosols (SIA) and black carbon to the

total PM mass between the two site locations, although more  $\text{NH}_4^+$  events are observed in the SIA at Chilbolton. Background concentrations of  $\text{NH}_3$  at both sites reflect the presence of mixed farmland; however the contribution of very strong local sources to the south-west of Chilbolton cause the large increase in annual average between sites.

In conclusion, when considering long-term regional trends based on the southern UK supersite data, the increase in  $\text{NO}_x$  and  $\text{NH}_3$  at Chilbolton must be taken into account and the Harwell and Chilbolton datasets should be treated separately.

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## References

- Abdalmogith S S and Harrison R M 2006 An analysis of spatial and temporal properties of daily sulfate, nitrate and chloride concentrations at UK urban and rural sites *J. Environ. Monit.* **8** 691–9
- AQEG 2004 *Nitrogen Dioxide in the UK* UK Department for Environment, Food and Rural Affairs <https://uk-air.defra.gov.uk/assets/documents/reports/aqeg/nd-summary.pdf>
- Beirle S, Boersma K F, Platt U, Lawrence M G and Wagner T 2011 Megacity emissions and lifetimes of nitrogen oxides probed from space *Science* **333** 1737–9
- Cape J N 2009 *Operation of EMEP 'Supersites' in the United Kingdom: Annual Report for 2007* UK Department for Environment, Food and Rural Affairs [https://uk-air.defra.gov.uk/assets/documents/reports/cat05/1003151149\\_EMEP\\_Supersite\\_Annual\\_report\\_to\\_Defra\\_for\\_2007.pdf](https://uk-air.defra.gov.uk/assets/documents/reports/cat05/1003151149_EMEP_Supersite_Annual_report_to_Defra_for_2007.pdf)
- Carslaw D C 2017 deweather: Remove the influence of weather on air quality data (R package version 0.4) <https://github.com/davidcarslaw/deweather>
- Carslaw D C 2018 worldmet: Import Surface Meteorological Data from NOAA Integrated Surface Database (R package version 0.8.6) <http://github.com/davidcarslaw/worldmet>
- Carslaw D C and Taylor P J 2009 Analysis of air pollution data at a mixed source location using boosted regression trees *Atmos. Environ.* **43** 3563–70
- Science and Technology Facilities Council (STFC) Chilbolton Facility for Atmospheric and Radio Research Natural Environment Research Council (NERC), Wrench C L 2003 Meteorological Sensor Data, Chilbolton Site (NCAS British Atmospheric Data Centre) <http://catalogue.ceda.ac.uk/uuid/45b25a7c531563f4422afcaeea0f07a7>
- Dammers E, Schaap M, Haaima M, Palm M, Kruit R J W, Volten H, Hensen A, Swart D and Erisman J W 2017 Measuring atmospheric ammonia with remote sensing campaign: Part I.—Characterisation of vertical ammonia concentration profile in the centre of The Netherlands *Atmos. Environ.* **169** 97–112
- Defra 2015 *Air Pollution in the UK 2014* UK Department for Environment, Food and Rural Affairs [https://uk-air.defra.gov.uk/assets/documents/annualreport/air\\_pollution\\_uk\\_2014\\_issue\\_1.pdf](https://uk-air.defra.gov.uk/assets/documents/annualreport/air_pollution_uk_2014_issue_1.pdf)
- Defra 2016 *Air Pollution in the UK 2015* UK Department for Environment, Food and Rural Affairs [https://uk-air.defra.gov.uk/assets/documents/annualreport/air\\_pollution\\_uk\\_2015\\_issue\\_1.pdf](https://uk-air.defra.gov.uk/assets/documents/annualreport/air_pollution_uk_2015_issue_1.pdf)
- Defra 2017 *Air Pollution in the UK 2016* UK Department for Environment, Food and Rural Affairs [https://uk-air.defra.gov.uk/assets/documents/annualreport/air\\_pollution\\_uk\\_2016\\_issue\\_1.pdf](https://uk-air.defra.gov.uk/assets/documents/annualreport/air_pollution_uk_2016_issue_1.pdf)
- Defra 2018a UK AIR: Site Information for Auchencorth Moss [https://uk-air.defra.gov.uk/networks/site-info?site\\_id=ACTH](https://uk-air.defra.gov.uk/networks/site-info?site_id=ACTH)
- Defra 2018b UK AIR: Site Information for Chilbolton Observatory [https://uk-air.defra.gov.uk/networks/site-info?site\\_id=CHBO](https://uk-air.defra.gov.uk/networks/site-info?site_id=CHBO)
- Elith J, Leathwick J R and Hastie T 2008 A working guide to boosted regression trees *J. Anim. Ecol.* **77** 802–13
- EMEP 2007 *Manual for Sampling and Chemical Analysis* (Kjeller: Norwegian Institute for Air Research) <http://nilu.no/projects/ccc/manual/index.html>
- European Parliament and Council of the European Union 2008 Directive 2008/50/EC on ambient air quality and cleaner air quality and cleaner air for Europe (Brussels, Belgium)
- Fagerli H and Aas W 2008 Trends of nitrogen in air and precipitation: model results and observations at EMEP sites in Europe, 1980–2003 *Environ. Pollut.* **154** 448–61



- Flecharad C R and Fowler D 1998 Atmospheric ammonia at a moorland site: I. The meteorological control of ambient ammonia concentrations and the influence of local sources *Q. J. R. Meteorol. Soc.* **124** 733–57
- Friedman J H 2002 Stochastic gradient boosting *Comput. Stat. Data Anal.* **38** 367–78
- Grange S K, Carslaw D C, Lewis A C, Boleti E and Hueglin C 2018 Random forest meteorological normalisation models for Swiss PM<sub>10</sub> trend analysis *Atmos. Chem. Phys.* **18** 6223–39
- Joly M and Peuch V H 2012 Objective classification of air quality monitoring sites over Europe *Atmos. Environ.* **47** 111–23
- Kuhlbusch T A J *et al* 2014 New directions: The future of European urban air quality monitoring *Atmos. Environ.* **87** 258–60
- Makkonen U, Virkkula A, Mäntykenttä J, Hakola H, Keronen P, Vakkari V and Aalto P P 2012 Semi-continuous gas and inorganic aerosol measurements at a Finnish urban site: comparisons with filters, nitrogen in aerosol and gas phases, and aerosol acidity *Atmos. Chem. Phys.* **12** 5617–31
- Malley C S, Braban C F and Heal M R 2014 The application of hierarchical cluster analysis and non-negative matrix factorization to European atmospheric monitoring site classification *Atmos. Res.* **138** 30–40
- Malley C S, Heal M R and Braban C F 2016 Insights from a chronology of the development of atmospheric composition monitoring networks since the 1800s *Atmosphere* **7** 160
- NOAA 2018 National Oceanic and Atmospheric Administration (NOAA) Integrated Surface Database (ISD) <https://ncdc.noaa.gov/isd>
- Pope R and Wu J 2014 A multi-objective assessment of an air quality monitoring network using environmental, economic and social indicators and GIS-based models *J. Air Waste Manage. Assoc.* **64** 721–37
- RoTAP 2012 Review of Transboundary Air Pollution (RoTAP): acidification, eutrophication, ground level ozone and heavy metals in the UK, a report for the UK Department for Environment, Food and Rural Affairs [https://uk-air.defra.gov.uk/library/reports?report\\_id=701](https://uk-air.defra.gov.uk/library/reports?report_id=701)
- Sather M E *et al* 2008 Baseline ambient gaseous ammonia concentrations in the four corners area and eastern Oklahoma, USA *J. Environ. Monit.* **10** 1319–25
- Spangl W, Schneider J, Moosmann L and Nagi C 2007 *Representativeness and classification of air quality monitoring stations* German Environment Agency (Umweltbundesamt) <http://www.umweltbundesamt.at/fileadmin/site/publikationen/rep0121.pdf>
- Stieger B *et al* 2018 Measurements of PM<sub>10</sub> ions and trace gases with the online system MARGA at the research station Melpitz in Germany – A five-year study *J. Atmos. Chem.* **75** 33–70
- Sutton M A, Howard C M, Erismann J W, Billen G, Bleeker A, Grennfelt P, van Grinsven H and Grizzetti B 2011 *European Nitrogen Assessment: Sources, Effects and Policy Perspectives* (Cambridge: Cambridge University Press)
- Tang Y S *et al* 2018 Drivers for spatial, temporal and long-term trends in atmospheric ammonia and ammonium in the UK *Atmos. Chem. Phys.* **18** 705–33
- Twigg M *et al* 2016 Impacts of the 2014–2015 Holuhraun eruption on the UK atmosphere *Atmos. Chem. Phys.* **16** 11415–31
- Twigg M M *et al* 2015 Water soluble aerosols and gases at a UK background site — Part 1: Controls of PM<sub>2.5</sub> and PM<sub>10</sub> aerosol composition *Atmos. Chem. Phys.* **15** 8131–45
- Tørseth K, Aas W, Breivik K, Fjæraa A M, Fiebig M, Hjellbrekke A G, Myhre C L, Solberg S and Yttri K E 2012 Introduction to the European monitoring and evaluation programme (EMEP) and observed atmospheric composition change during 1972–2009 *Atmos. Chem. Phys.* **12** 5447–81
- UK-AIR Data Selector 2018 UK Department for Environment, Food & Rural Affairs [https://uk-air.defra.gov.uk/data/data\\_selector](https://uk-air.defra.gov.uk/data/data_selector)
- UK-AIR Library 2018 UK Department for Environment, Food & Rural Affairs [https://uk-air.defra.gov.uk/library/reports?section\\_id=13](https://uk-air.defra.gov.uk/library/reports?section_id=13)
- UKEAP 2015 2015 *Annual Report* UK Department for Environment, Food and Rural Affairs [https://uk-air.defra.gov.uk/assets/documents/reports/cat13/1611101001\\_UKEAP\\_annual\\_report\\_2015\\_Ricardo\\_Issue\\_2.pdf](https://uk-air.defra.gov.uk/assets/documents/reports/cat13/1611101001_UKEAP_annual_report_2015_Ricardo_Issue_2.pdf)
- UNECE 2004a *Handbook for the 1979 Convention on Long-Range Transboundary Air Pollution and its Protocols* (Geneva, Switzerland: United Nations Economic Commissions for Europe) <http://www.unece.org/fileadmin/DAM/env/lrtap/ExecutiveBody/Handbbok.E.pdf>
- UNECE 2004b *The EMEP Monitoring Strategy and measurement programme 2004–2009* United Nations Economic Commissions for Europe [http://www.unece.org/fileadmin/DAM/env/lrtap/emep/Monitoring%20Strategy\\_full.pdf](http://www.unece.org/fileadmin/DAM/env/lrtap/emep/Monitoring%20Strategy_full.pdf)
- Vieno M *et al* 2016 The UK particulate matter air pollution episode of March–April 2014: more than Saharan dust *Environ. Res. Lett.* **11** 059501
- Vieno M, Dore A J, Bealey W J, Stevenson D S and Sutton M A 2010 The importance of source configuration in quantifying footprints of regional atmospheric sulphur deposition *Sci. Total Environ.* **408** 985–95
- Vogt E *et al* 2013 Heterogeneity of atmospheric ammonia at the landscape scale and consequences for environmental impact assessment *Environ. Pollut.* **179** 120–31
- WHO 2006 *Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide, Global update 2005: Summary of risk assessment* World Health Organisation (WHO) [http://whqlibdoc.who.int/hq/2006/WHO\\_SDE\\_PHE\\_OEH\\_06.02\\_eng.pdf?ua=1](http://whqlibdoc.who.int/hq/2006/WHO_SDE_PHE_OEH_06.02_eng.pdf?ua=1)
- WHO 2013 *Review of Evidence on Health Aspects of air Pollution — REVIHAAP Project: Technical Report* World Health Organisation (WHO) available at: [http://euro.who.int/\\_\\_data/assets/pdf\\_file/0004/193108/REVIHAAP-Final-technical-report-final-version.pdf](http://euro.who.int/__data/assets/pdf_file/0004/193108/REVIHAAP-Final-technical-report-final-version.pdf)